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DIRECT-WRITE ASSEMBLY OF FUNCTIONAL INKS FOR PLANAR AND 3D MICROSTRUCTURES

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ABSTRACT

The ability to pattern functional inks with high-speed and low-cost printing techniques is required for many emerging applications including sensors, displays, solar cells, and antennas. Direct-write assembly is a low-cost, mask-less printing route that enables rapid design and patterning of planar and three-dimensional (3D) structures. In this filamentary printing approach, a concentrated ink with tailored rheological properties is extruded through a micronozzle(s) that is translated using a three-axis positioning stage. The ink rapidly solidifies to maintain its shape so that spanning or free-standing structures can be deposited both in- and out-of-plane. With this approach, we aim to demonstrate multi-scale (e.g., from the nano- to macro- length scales) assembly of complex 3D structures composed of multiple materials (e.g., polymers, metals, and ceramics). Here, we present our recent work on developing functional metallic inks for printing planar and 3D conductive microstructures for stacked chips, light emitting diodes (LEDs), and printed antennas.

KEYWORDS: Direct-Write, Functional Inks, Printed Electronics, Three-Dimensional Printing

INTRODUCTION

There is considerable interest in fabricating low-cost, printed electronics and optoelectronics for many emerging applications, including sensors, displays, solar cells, and antennas. Direct-write techniques offer an attractive alternative to conventional lithography, due to the low-cost of the printing equipment, ease of manufacture, simplicity, and flexibility in material systems, dimensions, and designs. For example, screen printing and inkjet printing have been extensively investigated for patterning a wide variety of functional inks on both rigid and flexible substrates. In addition, large-area patterning may be achieved by roll-to-roll processes commonly used in the graphics arts industry, such as flexographic, gravure, and off-set printing. However, these techniques suffer from several limitations, including their inability to create features with lateral dimensions below 10 μm [1]. In addition, they are generally restricted to printing planar, low-aspect ratio features that must be supported by the underlying substrate or printed material, making it impossible to pattern spanning elements in- or out-of-plane. Hence, it is of both scientific and technological interest to develop alternative printing approaches that enable fine features to be patterned in both planar and complex 3D forms.

Direct-write assembly is a layer-by-layer printing technique, in which concentrated inks are printed in arbitrary planar and 3D forms with lateral dimensions (minimum ~200 nm) that are at least an order of magnitude lower than those achieved by conventional printing methods [2]. A schematic diagram of this process is shown in Figure 1. Paramount to this approach is the creation of concentrated inks that can be extruded through fine deposition nozzles as filament(s), which then undergo rapid solidification to maintain their shape even as they span gaps across unsupported regions. Important rheological parameters for a given ink design include its viscosity, viscoelastic properties (i.e., the shear loss and elastic moduli), and solidification behavior. These parameters are tailored for the particular application and print conditions. To date, direct-write assembly has been demonstrated with a wide variety of functional inks, including colloidal gels [3], organic waxes [4], concentrated polyelectrolyte complexes [5], silk [6], and sol-gel materials [7]. These inks solidify either through liquid evaporation, gelation, or temperature- or solvent-induced phase changes.

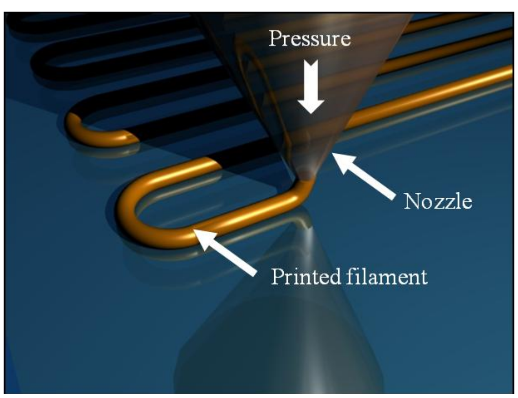

Figure 1: Schematic illustration of the direct-write assembly process.

Conductive metallic inks are of great interest for printed electronics applications. The ability to pattern low resistance, metallic electrodes with fine resolution in high aspect ratio layouts, and possibly spanning three dimensions, is a technologically important goal. Many applications, including solar cell metallization, interconnects for LEDs and displays, and printed antennas would benefit from this capability. With this in mind, the focus of this paper is the design and development of metallic nanoparticle inks for direct-write assembly of functional devices in planar and 3D layouts.

EXPERIMENTAL

Ink synthesis: The complete details of the silver ink preparation and synthesis can be found in Reference [8]. Silver nanoparticle ink is prepared by dissolving 2 g poly(acrylic acid) (PAA) solution (50 wt% polymer in water, Mw = 5,000 g/mol), 1 g PAA (25 wt% polymer in water, Mw = 50,000 g/mol), and 40 g diethanolamine (DEA) in 50 ml of H_2O, while stirring for 2 h in a water bath at room temperature. A silver nitrate solution (20 g $AgNO_3$ in 20 ml H_2O) is then added to this solution, while vigorously stirring, to yield weight ratios of DEA/Ag and PAA/Ag of 3.15 and 0.089, respectively. The resulting reddish-yellow solution is then gently stirred for 24 h at room temperature. The solution exhibits a gradual color change from reddish-yellow to dark black, which coincides with the formation of silver nanoparticles that are ~5 nm.

The silver nanoparticles are ripened by sonicating the solution in a heated water bath at 60°C for 2 h. After this step, the mean particle size is ~20 ± 5 nm with a size distribution between 5 – 50 nm. The resulting silver nanoparticles are concentrated by titrating 240 ml ethanol at 10 ml min^{-1}. Because ethanol is a poor solvent for the PAA-coated silver nanoparticles, rapid coagulation ensues. After decanting the supernatant, the coagulated ink is centrifuged at 9,000 rpm for 20 min to remove excess solvent and recover the precipitate. The process yields a highly concentrated silver nanoparticle ink with a solids loading of ~81 wt%. The resultant ink is then homogenized by adding ~10 wt% of a humectant solution (30 wt% ethylene glycol/70 wt% water) followed by deairing for ~30 min under a light vacuum (ca. 25 mbar) until bubble formation ceases. After homogenization, the ink changes from a bluish to a magenta color.

Printing process for interconnects: Direct-write assembly is carried out using a 3-axis micropositioning stage whose motion is controlled by computer-aided design software. The silver ink is housed in a syringe (3 mL barrel, EFD Inc., East Providence, RI) attached by luer-lok to a borosilicate micronozzle (diameter = 1 – 30 μm produced using a micropipette puller (P-2000, Sutter Instrument Co., Novato, CA). An air-powered fluid dispenser is used to pressurize the barrel and control the ink flow rate. The required pressure depends upon ink rheology, nozzle diameter, and printing speed, but typical values range from 10 – 100 psi at 20 – 500 μm s^{-1}. Direct-write assembly is performed in air under ambient conditions at a relative humidity of 20 – 30% at a temperature of 23 – 26°C. After printing, each structure is heat treated in air, typically between 200 – 550°C, to form conductive silver microstructures.

Printing process for electrically small antennas: Concentrated silver nanoparticle ink (~72 wt% silver) is loaded into a micronozzle (100 μm inner diameter, Nordson EFD) and mounted onto a three-axis positioning stage. The 1.2 mm thick glass hemisphere (Pyrex® 7740, Ace Glass) is affixed to a glass slide, centered onto a precision rotation stage (sensitivity = 15 arc s, Newport), and secured to the stage. The hemisphere is aligned in the *xy*-plane to the nozzle by performing consecutive circular revolutions at the base (with radius equal to the radius of the hemisphere plus the nozzle diameter) until minimal or no contact is made between the nozzle and hemisphere. Markers are printed onto the glass slide at intervals demarcating start points for each arm. A design file for the printing stage control program is generated with custom computer-aided design software.

After substrate alignment, each antenna is conformally printed by loading the design file, executing, and programming stop and start flow commands between each meanderline arms. In some cases, a bent micronozzle (bend angle = 10 – 45°) is used, which is loaded with ink, aligned to the markers and hemisphere, and a single arm is printed from a given start point. After finishing the arm and ceasing ink flow, the nozzle returns to the original start point, the hemisphere is precisely rotated to the next marker, and another arm is printed, continuing with additional arms in the same fashion. The approximate build time for a single antenna depends upon the design and print speed and ranges from roughly 30 min to 3 h. After printing, each antenna is heat treated to 550°C in air for 3 h to form highly conductive silver traces.

RESULTS AND DISCUSSION

We have created concentrated silver nanoparticle inks for patterning microelectrodes onto semiconductor, plastic, and glass substrates [8]. With this approach, wire bonding to three-dimensional devices, printing spanning interconnects for LEDs, and conformal printing of electrically small antennas have been demonstrated. In general, metallic nanoparticles are synthesized in solution by the reduction of metal precursors in the presence of stabilizing agents [9]. In our multi-step synthetic approach, highly concentrated silver nanoparticle inks are prepared using an aqueous system that contains silver nitrate as the silver precursor, poly(acrylic acid) (PAA) as the stabilizing agent, and diethanolamine as the reducing agent [8]. The components are first mixed under ambient conditions to create a population of very fine (~5 nm) silver nanoparticles. This particle population is ripened by heating the solution to 60°C. Ethanol, a poor solvent for the PAA-coated nanoparticles, is added to induce rapid particle coagulation. Next, the ink is centrifuged to achieve the desired solids loading (70 – 85 wt% silver nanoparticles). Finally, ethylene glycol is added as a humectant, which allows the ink to be patterned in air without clogging.

We have synthesized a broad range of silver nanoparticle inks. Silver nanoparticle inks with solids loading between 70 – 85 wt%, mean particle size of 20 ± 5 nm, and particle size distribution between 5 – 50 nm exhibit both optimal flow behavior through fine deposition nozzles (1 – 30 μm) and low resistivity at modest annealing temperatures (≥ 200°C). We have observed the elastic modulus (G') for silver nanoparticle inks of varying solids loading rises nearly three orders of magnitude as the nanoparticle content increases from 60 to 75 wt%. From our observation, a minimum G' of 2,000 Pa is required to produce spanning features, which occurs at a silver nanoparticle concentrations ≥ 70 wt%. Similar behavior is observed for ink viscosity, which rises three orders of magnitude with increasing nanoparticle content from 10 to 85 wt%. The optimal concentration range for 3D printing is experimentally determined to be 70 – 85 wt%.

We find that these inks can span unsupported gaps that are extraordinarily wide and tall. For example, it is possible to vertically print microelectrodes with arbitrary height and angle (Figure 2) with feature sizes down to ~10 μm. Unlike conventional wire-bonding techniques, our approach allows fine silver microwires to be bonded using minimal contact pressure on both flat and curved surfaces, which is highly advantageous for delicate devices. In another example, we demonstrate 64 printed interconnects for a dummy stacked 3D chip (Figure 3). Importantly, with this approach we can print both spanning and conformal interconnects. In the latter approach, the ink would be conformally printed onto the chip sidewall, which is more structurally robust and leads to fewer packaging concerns. Figure 4 shows silver micro-arches printed on a gold pad (80 by 80 μm) on a LED pixel and the LED pixel emitting blue light under an applied bias of 2 V after annealing the microelectrodes at 200°C for 3 hours.

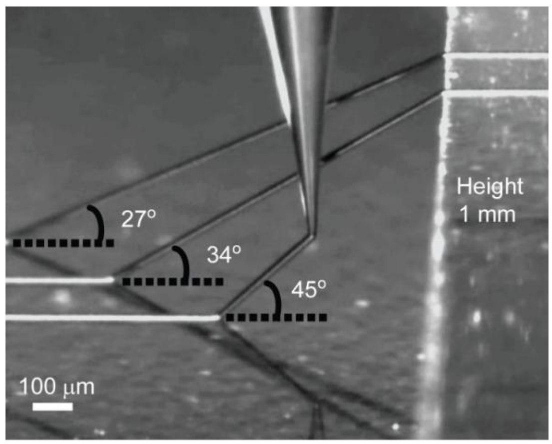

Figure 2: Optical image acquired during direct-write assembly of silver microelectrodes between two glass substrates offset by a 1 mm height difference.

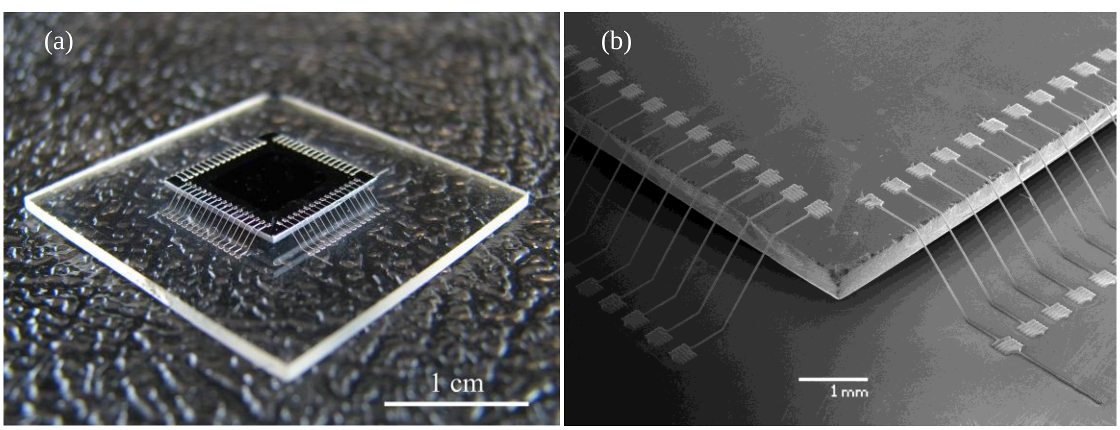

Figure 3: Printed interconnects for a dummy 3D stacked chip showing (a) low magnification digital photograph and (b) high magnification scanning electron micrograph.

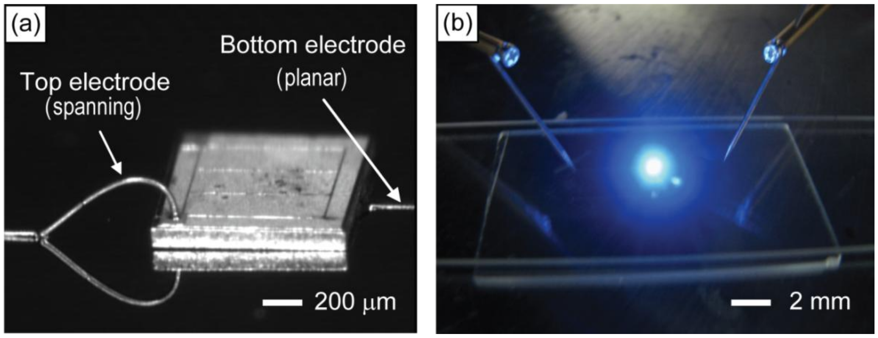

Figure 4: (a) Image of a LED chip (1 mm × 1 mm × 200 μm) connected by a bottom electrode composed of a silver pad with a planar line and a top electrode composed of a spanning silver microelectrode, both of which are patterned by direct-write assembly. (b) Image of the LED chip emitting blue light under an applied bias of 2 V after annealing at 200 °C for 3 h.

We have also exploited this silver nanoparticle ink to fabricate 3D electrically small antennas by conformal printing of metallic inks onto convex and concave hemispherical surfaces in the form of conductive meander lines (Figure 5) [10]. The antennas' bandwidth approaches the fundamental limit for their size, offering nearly an order of magnitude improvement over rudimentary monopole antenna designs. With this printing approach, antennas can be rapidly adapted to new specifications, including other operating frequencies, device sizes, or encapsulated designs that offer enhanced mechanical robustness.

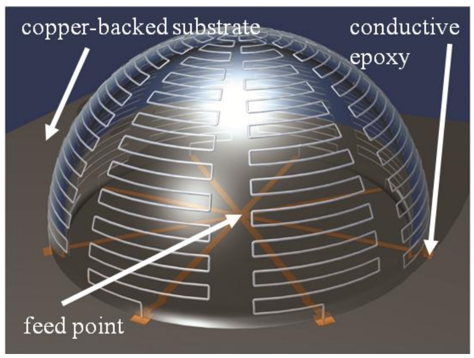

Figure 5: Schematic illustration of electrically small antennas conformally printed onto a glass hemisphere.

Figure 6(a) shows a representative antenna being patterned on the outer or convex surface of the glass hemisphere. The printed antenna consists of tapered silver meanderline "arms" that are affixed to patterned copper feedlines on a low-loss laminate substrate. The antenna's measured center frequency is 1.73 GHz with a 5.83:1 bandwidth of 15.2%. Importantly, this antenna exhibits excellent performance relative to the fundamental limits as well as good agreement with simulation [10]. We also conformally print an antenna on the interior or concave surface of the glass hemisphere. In this process, the glass hemisphere is embedded in a PDMS mold to hold it in place during printing. After printing is completed, the patterned structure is removed from the mold (Figure 6(b)). In this motif, the hollow glass hemisphere serves as a protective barrier, allowing the device to be easily handled and mounted on a low-loss laminate substrate. This antenna exhibits a center frequency of 1.70 GHz with bandwidth of 12.6%.

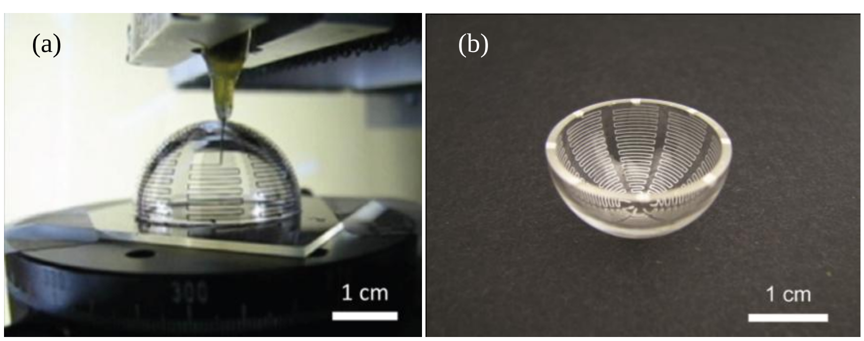

Figure 6: (a) Frame grab from a video captured during printing an electrically small antenna onto the convex surface of a hemisphere and (b) digital photograph of an electrically small antenna printed onto the concave surface of a hemisphere.

CONCLUSION

Concentrated silver nanoparticle inks have been created for direct-write assembly of conductive microelectrodes. By carefully controlling the silver nanoparticle concentration, size, and distribution, inks with high solids loading (≥ 70 wt%) are produced that are ideally suited for direct-write assembly. Self-supporting microelectrodes in either planar or 3D forms of arbitrary complexity are patterned on a wide variety of substrates. Using this technique, wire-bonding to stacked chips and patterning complex interconnects for LEDs are demonstrated. We have also demonstrated conformal printing of 3D electrically small antennas with excellent performance characteristics. Our design process, derived from fundamental principles, enables specification of both operating frequency and size, while achieving near-optimal bandwidth at several frequencies of interest for wireless communications.

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